

PROCESS RELATED EFFECTS ON THE CHEMICAL AND TOXICOLOGIC  
CHARACTERISTICS OF COAL DERIVED FUELS

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ABSTRACT

As a component of an ongoing program to assess the potential health effects of coal conversion materials, we have recently completed chemical and toxicologic studies of a sample set collected on selected days of a 25-day demonstration run of a catalytic two stage direct coal liquefaction (CTSL) process. There was an increase in heteroatomic, nitrogen containing polycyclic aromatic compounds (NPAC) and hydroxy-substituted PAC, compounds as the operation time of the pilot plant increased. The proportion of material which boiled above 975°F also increased in the solids-free portion of the recycle slurry oil as pilot plant operation time increased. As anticipated from the increase in NPAC concentration during the run, the microbial mutagenic activity of selected process materials also increased as a function of run time. Likewise, the tumorigenicity of the materials produced later in the demonstration run was higher than that of those produced initially. These results support the view that catalyst deactivation during the course of the run gives rise not only to lower coal conversion, but also to increased toxicologic activity.

INTRODUCTION

Chemical and toxicologic characteristics of direct coal liquefaction materials are highly dependent on the specific process by which the coal liquids were produced. Of particular importance are those process variables which can

affect the boiling point (bp) range and degree of hydrogenation of product materials (Wilson et al., 1986). Thus, process modifications such as recycle of heavy ends to extinction (Anderson and Free1, 1983), adjustment of product distillation upper temperature cut points to ca.  $< 650$  °F (Pelroy et al., 1985), incorporation of a catalytic hydrogenation step (Wilson et al, 1986), and, to a lesser extent, changes in feed coal type can reduce the toxicologic potential of coal liquefaction materials as determined by microbial mutagenicity testing and mouse skin tumorigenesis assays.

We have recently concluded studies that assessed the effects of process run time, and hence catalyst age, on the chemical composition and toxicologic activity of materials from an advanced coal liquefaction process. In the present paper, these results are reported and compared to data from earlier studies which dealt with other process variables such as those listed above. Studies of catalyst effects on toxicology will be important in the new petroleum resid/coal co-processing schemes, which will depend heavily on catalyst performance.

#### EXPERIMENTAL

During July of 1984, Hydrocarbon Research, Inc. (HRI) performed a 25-day demonstration run of their catalytic two-stage liquefaction coal conversion (CTSL) process at Lawrenceville, NJ. An objective of this CTSL process was to take advantage of catalytic reactions in both reactors to convert coal to a liquid; details of the CTSL process are given by Comolli et al. (1984) and Wright and Later (1985). Samples of the pressure filter liquid (PFL; the solids-free portion of the recycle slurry oil, an internal process stream material) were taken each day of the demonstration run. A product distillate blend (PDB), more representative of the actual net product from the CTSL process, was also supplied by HRI.

Chemical analyses were performed on fractions isolated from the PFL and PDB materials by adsorption column chromatography (Later et al. 1981). Chemical class fractions of aliphatic hydrocarbons (AH), polycyclic aromatic hydro-

carbons (PAH), nitrogen-containing polycyclic aromatic compounds (NPAC), and hydroxy-substituted PAH (hydroxy-PAH) were produced using neutral alumina as an adsorbent. Due to the high concentration of hydrogenated and partially hydrogenated components present in these samples, the hydroaromatic compounds were isolated using picric-acid-coated alumina as an adsorbent (Wozniak and Hites, 1983). Selected chemical fractions isolated from the PFL and PDB materials were then analyzed by high-resolution gas chromatography (HRGC), gas chromatography/mass spectrometry (GC/MS), and low-voltage probe-inlet mass spectrometry (LVMS).

The mutagenic response of all crude samples and chemical class fractions were measured using the histidine reversion microbial mutagenicity test with Salmonella typhimurium, TA98 (Ames et al., 1975). Selected crudes were tested for tumorigenic potential using the initiation/promotion (I/P) assay for tumorigenicity in mouse skin (Mahlum, 1983). Details regarding the methods of chemical analyses and measurement of toxicologic activity in the CTSL materials are given by Wright and Later (1985).

## RESULTS AND DISCUSSION

### Chemical Analysis

The distillation weight percent distribution of the CTSL PFL materials from days 5, 10, 15, 19, and 24 are given in Table 1. The composition boiling above 975°F increased significantly over the duration of the demonstration run. There was a concurrent decrease in the composition which distilled less than

TABLE 1. Distillation Data for Selected PFL Sample Materials

Distillation Temperature	Weight Percent Composition				
	Day 5	Day 10	Day 15	Day 19	Day 24
IBP - 650°F	28.1	21.0	18.9	14.9	13.1
650 - 850°F	33.4	32.7	30.9	31.8	30.9
850 - 975°F	11.4	12.7	13.8	8.7	6.8
975°F+	27.1	33.6	36.4	44.6	49.2

650°F. The increase in higher boiling constituents of the PFL may be an effect of catalyst deactivation and recycle oil boiling point adjustment.

Elemental analysis data indicated there were changes in the PFL composition during the course of the 25-day demonstration run. These changes included a general decrease in the carbon content of the PFL material and an increase in the heteroatom content with catalyst age and duration of the run. The nitrogen content increased gradually from 0.61 weight percent on day 5 to 0.99 weight percent on day 24; the sulfur content increased similarly from 0.046 to 0.186 weight percent for the same days of pilot plant operation.

The chemical class composition (as determined by alumina column chromatography) of the PFL materials from days 1, 5, 10, 15, 19, and 24 are shown in Figure 1. As the demonstration run progressed, the PFL AH composition decreased by more than a factor of two, the PAH composition of the PFL materials was fairly constant, and both the NPAC and hydroxy-PAH fractions showed significant increases. The PDB had a significantly higher AH

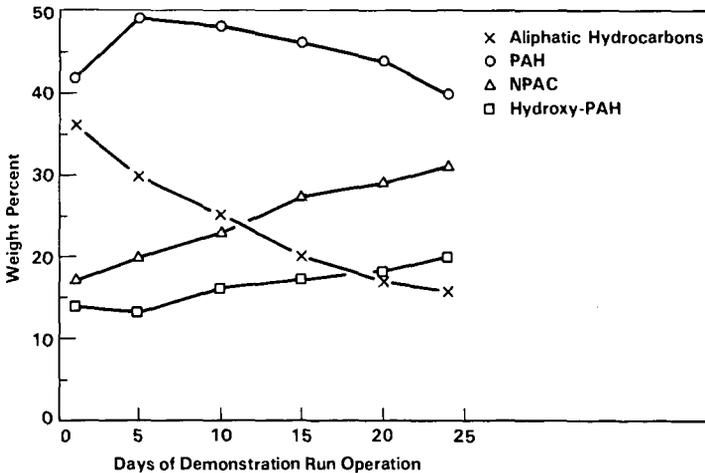


FIGURE 1. Chemical Class Composition of CTSL Pressure Filter Liquid Samples as Determined by Alumina Column Chromatography

composition and significantly lower PAH, NPAC, and hydroxy-PAH composition than did the PFL material. The PDB contained 43% AH, 23% PAH, 5.2% NPAC, and 6.7% hydroxy-PAH by weight as determined by alumina column chromatography.

The hydroaromatic composition of the CTSL PFL materials from days 1, 5, 10, 15, 19, and 24 is shown in Figure 2. The AH of fraction PA1 and the hydroaromatic compounds of fraction PA2 generally decreased as the operation time of the demonstration run increased. The dihydro- and less-than-three-ringed PAH composition of fraction PA3 was constant after about day 5 of the demonstration run. In addition, the greater-than-three ringed PAH and some slightly polar compounds of fraction PA4 generally increased with increasing operation time. Indan, tetralin, and hydrogenated acenaphthylenes, fluorenes, phenanthrenes, fluoranthenes, and pyrenes were detected as major components in the hydroaromatic fraction of the PDB when analyzed by HRGC and GC/MS. Alkylated species of each of the above were also detected in the PA2 fraction.

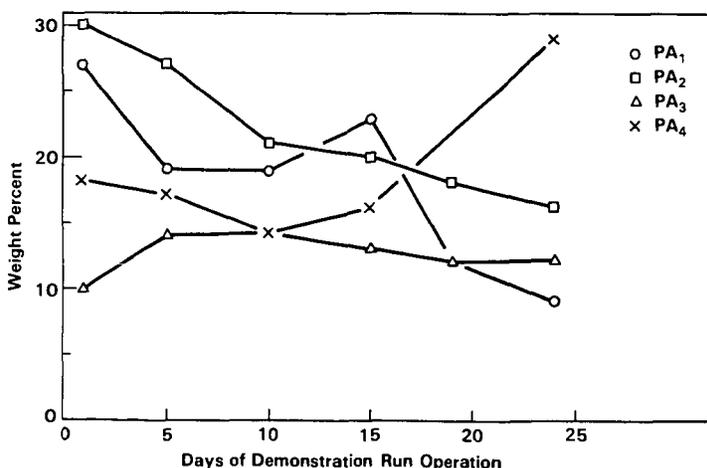


FIGURE 2. Hydroaromatic Composition of CTSL Pressure Filter Liquid Samples as Determined by Picric-Acid-Doped Column Chromatography

The PAH and NPAC fractions were analyzed in detail since these chemical class fractions have been previously shown to be the most tumorigenic and mutagenic fractions in coal-derived materials, respectively. The quantitative HRGC results for over 50 components in the PAH fractions and 40 components in the NPAC fractions of the PFL materials from day 1, 5, 10, 15, 19, and 24 are given by Wright and Later (1985). The results of the PAH fraction analyses can be summarized by the data given in Figure 3. The quantitative values for some low molecular weight PAH in the isolated PAH fractions, i.e. the methylnaphthalenes and two isomers of dimethylnaphthalene, were summed and are plotted for each of the PFL materials analyzed. The concentration of these low molecular weight components decreased over the duration of the demonstration run. The quantitative values for some of the high molecular weight PAH in the isolated PAH fractions, i.e. two methylchrysene isomers, the benzofluoranthenes, the benzopyrenes, indeno(1,2,3-cd)pyrene, and benzo(ghi)perylene, were also summed and are plotted in Figure 3 for each of the PFL materials analyzed. The

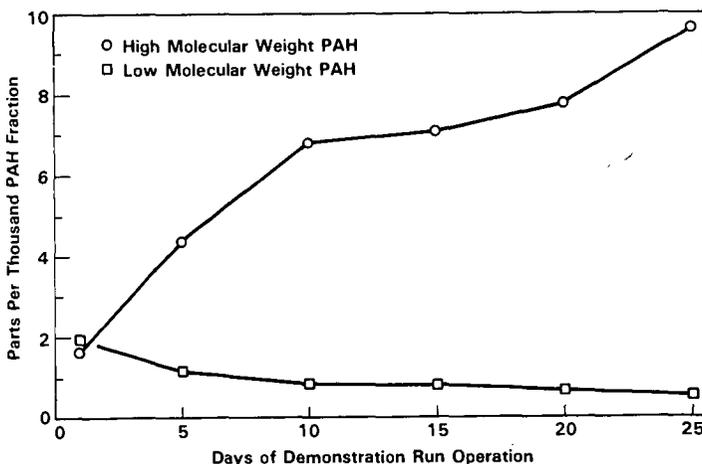


FIGURE 3. Concentrations (parts per thousand) of Selected High Molecular Weight Components and Low Molecular Weight Components in PAH Fractions of Selected CTSL PFL Samples

concentration of these high molecular weight components increased significantly with increasing pilot plant operation time. Operating temperatures were equilibrated during the first 3 days of the demonstration run; the composition of the PAH fractions continued to change after operating temperatures were equilibrated at day 3. These changes may be an effect of catalyst degradation or an effect of the resid recycle. Similar increases in higher molecular weight composition were noted for the AH, NPAC, and hydroxy-PAH chemical class fractions when analyzed by LVMS.

The individual components in the chemical class fractions of the PDB were similar to those found in the PFL materials, only for a lower molecular weight range. The quantitative analyses of the PDB and the PFL composite revealed that the concentration of the methylnaphthalenes and two dimethylnaphthalene isomers was more than an order of magnitude higher in the PDB as compared to the PFL, for example.

To compare the degree of alkylation of the CTSL PDB to products from other coal liquefaction processes, the quantitative values for the following compounds were summed and were then divided by the quantitative values of their respective parent compounds: the methylphenanthrene isomers, the methylcarbazole isomers, and 1-methyl pyrene. The resulting ratios were then summed. The summed ratios of these quantitative values are given in Table 2 for the CTSL PDB as well as solvent refined coal (SRC)-I, SRC-II, H-Coal, EDS, integrated two-stage liquefaction (ITSL) (Lummus), ITSL (Wilsonville), and nonintegrated two-stage liquefaction (NTSL) products. The single-stage, noncatalytic SRC materials showed the lowest degree of alkylation compared to the single-stage, catalytic H-Coal, hybrid EDS, or any of the two-stage coal liquefaction products. The highest degrees of alkylation were present in the two-stage coal liquefaction materials. Both ITSL, the NTSL, and the CTSL materials showed similar degrees of alkylation to each other, as determined by these means.

Those processes which incorporated catalysts had higher degrees of hydrogenation than did the noncatalytic processes. Quantitative values for the 1,2-dihydrophenalene and a dihydrofluoranthene were divided by the quantitative values of fluorene and fluoranthene, respectively, to compare the degree of hydrogenation of coal liquefaction process materials. These two ratios were

**TABLE 2.** Relative Degrees of Alkylation and Hydrogenation of Coal Liquefaction Materials as Determined by HRGC Analysis

<u>Coal Liquefaction Process</u>	<u>Relative Degree of Alkylation<sup>(a)</sup></u>	<u>Relative Degree of Hydrogenation<sup>(a)</sup></u>
SRC-I	1.3	0.2
SRC-II	1.7	0.6
H-Coal	3.2	4.2
EDS	3.4	4.4
ITSL Lummus	4.6	6.3
ITSL Wilsonville	4.4	6.0
NTSL Wilsonville	4.9	11
CTSL PDB	4.1	10

(a) See text for explanation.

then summed and are also given for each of the coal liquefaction materials in Table 2. The CTSL PDB and NTSL product showed the highest degree of hydrogenation, as determined by this method.

#### Biological Testing

The microbial mutagenicity results indicated a general trend of increasing mutagenicity with increased pilot plant operation time. The results of testing crude PFL materials from each day of the demonstration run were as follows: the responses, in rev/ $\mu$ g, ranged from approximately 1 to 2 for the first 5 days, 2 to 3 rev/ $\mu$ g for the next 5 days, 4 to 6 rev/ $\mu$ g for days 11 through 15, 6 to 10 rev/ $\mu$ g for days 16 through 20, and 9 to 12 rev/ $\mu$ g for the last 5 days of the demonstration run. The trend of increasing mutagenic response with time of operation correlates with the chemistry analysis data, which showed that the PFL materials had an increasing heteroatomic (particularly NPAC) composition as the length of pilot plant operation time increased. The microbial mutagenic response of coal liquefaction materials has historically been related to the NPAC chemical class fractions of coal liquefaction materials analyzed using these methods.

The CTSL PDB had a microbial mutagenicity dose response of 1.7 rev/ $\mu$ g with S. typhimurium, TA98. This response was higher than materials representative of Wilsonville (bp >450°F) and Lummus (bp >400°F) ITSL final products: approximately 2 rev/ $\mu$ g for the CTSL versus 0 rev/ $\mu$ g for the ITSL materials. The PDB did, however, have a lower mutagenic response than that of a NTSL (bp >450°F) final product (6 rev/ $\mu$ g). The majority of microbial mutagenicity of all the CTSL materials tested was associated with the NPAC fractions when the chemical class fractions were tested with S. typhimurium, TA98. These results were consistent with other coal liquefaction materials studied to date.

The results are given in Table 3 for the I/P mouse skin tumorigenicity assay of days 5, 15, and 24 PFL materials from the 25-day demonstration run of the HRI CTSL process. The mean number of tumors per mouse data (normalized to a population of 30 mice) indicated a general trend of increasing tumorigenicity with increasing length of pilot plant operation and catalyst deactivation. These I/P results were in general agreement with the chemistry results that showed that the PFL materials had decreased AH content and increased molecular weight distribution with increasing length of pilot plant operation. The percent tumor incidences were similar for all the PFL materials tested

TABLE 3. I/P Results (mean number of tumors per mouse) for Selected Coal Liquefaction Materials

Sample	Nominal bp Range (°F)	Tumors/Mouse <sup>(a)</sup>
CTSL PFL, Day 5	500 - 975+	1.37
CTSL PFL, Day 15	500 - 975+	1.62
CTSL PFL, Day 24	500 - 975+	2.27
CTSL PDB	<850	0.57
ITSL Second-Stage Product (Wilsonville)	450 - 850+	1.3
NTSL Second-Stage Product (Wilsonville)	450 - 850+	1.1
ITSL TLP (Lummus)	~400 - 850+	2.6

(a) Normalized to 30 mice per test material.

(approximately 70% after 191 days); however, day 5 results were slightly lower (~62%) and day 15 results were slightly higher (~75%) than the rest.

The skin-tumor initiating activity of the PDB (also given in Table 3 in terms of mean number of tumors per mouse) was significantly less than that of any of the PFL materials tested when judged by either tumor yield or tumor incidence; this is predictable from the significantly increased bp range of the PFL (>975°F) versus that of the PDB (<850°F) materials. Increasing tumorigenicity has been noted with increasing bp of coal liquefaction materials by Wright *et al.* (1985).

Also included in Table 3 are the mean number of tumors per mouse for the ITSL and NTSL materials, with nominal bp information for all samples. The CTSL PDB appeared to have less tumor initiating activity than did the NTSL or ITSL products, probably an effect of the lower bp of the former versus the latter.

#### ACKNOWLEDGMENT

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